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PCT/JP00/00210  
-filed January 19, 2000

Re: Application of Kiyoshi IWANAGA, Tetsuya SUZUTA, Yasuhiko MORI, and  
Masayuki YOSHII  
PROCESS FOR PRODUCING CHLORINE  
Assignee: SUMITOMO CHEMICAL COMPANY, LIMITED  
Our Ref: Q65479

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty:

- ☒ an executed Declaration and Power of Attorney.
- ☒ an English translation of the International Application.
- ☒ an executed Assignment and PTO 1595 form.
- ☒ an International Search Report and a Form PTO-1449 listing the ISR references.
- ☒ the Notification Concerning Submission or Transmittal of Priority Document.

It is assumed that copies of the International Application, the International Preliminary Examination Report, and any Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

The Government filing fee is calculated as follows:

Total claims	<u>12</u>	-	20	=	<u>          </u>	x	\$18.00	=	<u>          </u>	\$0.00
Independent claims	<u>1</u>	-	3	=	<u>          </u>	x	\$80.00	=	<u>          </u>	\$0.00
Base Fee										\$860.00

**TOTAL FILING FEE**

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<u>\$860.00</u>
<u>\$ 40.00</u>
<u>\$900.00</u>

Checks for the statutory filing fee of \$860.00 and Assignment recordation fee of \$40.00 are attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from January 22, 1999 based on Japanese Application No. 014236/1999.

Respectfully submitted,

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Registration No. 33,725

BEK:rw1

## DESCRIPTION

PROCESS FOR PRODUCING CHLORINE

## Field of the Invention

5       The present invention relates to a process for  
producing chlorine. In particular, the present invention  
relates to a process for producing chlorine comprising  
oxidizing hydrogen chloride in a gas containing hydrogen  
chloride with a gas containing oxygen.

## Background Art

10       Chlorine is a useful raw material for the production of  
vinyl chloride, phosgene, etc. and it is well known that  
chlorine is obtained through the oxidization of hydrogen  
15       chloride. For example, a process comprising catalytically  
oxidizing hydrogen chloride with molecular oxygen in the  
presence of a catalyst to obtain chlorine is known. With  
this process, a copper base catalyst, which is called a  
Deacon catalyst, is known to have a good catalytic activity,  
20       and various Deacon catalysts comprising copper chloride,  
potassium chloride and various kinds of compounds as third  
components are proposed. Besides the Deacon catalysts,  
processes using chromium oxide or its compound, or a  
ruthenium oxide or its compound, as a catalyst are also  
25       proposed.

However, since the oxidation reaction of hydrogen chloride is an exothermic reaction with 59 kJ/mol-chlorine, it is important to suppress excessive hot spot in a layer packed with the catalyst from the viewpoint of reducing the thermal degradation of the catalyst and maintaining the stability and easiness of operation. Furthermore, the excessive hot spot may induce a runaway reaction in the worst case, or the high temperature gas corrosion of a reactor material may be caused with hydrogen chloride and/or chlorine.

"Catalyst" Vol. 33, No. 1 (1991) describes that, in the reaction of pure hydrogen chloride with pure oxygen in the presence of chromium oxide as a catalyst, it is difficult to remove the hot spot in a fixed bed reaction system, and that it is necessary to use a fluidized bed reactor in a practical apparatus.

#### Disclosure of Invention

Under such circumstances, one object of the present invention is to provide a process for producing chlorine comprising oxidizing hydrogen chloride in a gas containing hydrogen chloride with a gas containing oxygen, in which the stable activity of the catalyst is maintained by suppressing the excessive hot spot in the catalyst-packed layer and making effective use of the catalyst-packed layer,

and which is very advantageous from the viewpoint of a catalyst cost, an equipment cost, an operation cost, and the stability and easiness of the operation.

According to the present invention, this object can be achieved by a process for producing chlorine comprising the step of oxidizing hydrogen chloride in a gas containing hydrogen chloride with a gas containing oxygen in the presence of a catalyst, wherein the oxidation of hydrogen chloride is carried out in at least two reaction zones each comprising a catalyst-packed layer, which are arranged in series, and a temperature in at least one of said reaction zones is controlled with a heat exchange system.

#### Embodiments for Carrying Out the Invention

As a gas containing hydrogen chloride to be used in the present invention, any gas containing hydrogen chloride, that is generated through a pyrolysis or combustion reaction of chlorine-containing compounds, a phosgeniting dehydrogen chlorination or chlorination reaction of organic compounds, combustion in an incinerator, etc., may be used.

The concentration of hydrogen chloride in the gas containing hydrogen chloride is usually at least 10 % by volume, preferably at least 50 % by volume, more preferably at least 80 % by volume. When the concentration of hydrogen chloride is less than 10 % by volume, the

separation of chlorine formed, and/or the recycling in the case of recycling unreacted oxygen may become complicated.

Components other than hydrogen chloride, which are contained in the gas containing hydrogen chloride, include aromatic chlorohydrocarbons (e.g. o-dichlorobenzene, monochlorobenzene, etc.), aromatic hydrocarbons (e.g. toluene, benzene, etc.), aliphatic chlorohydrocarbons (e.g. vinyl chloride, 1,2-dichloroethane, methyl chloride, ethyl chloride, propyl chloride, allyl chloride, etc.), aliphatic hydrocarbons (e.g. methane, acetylene, ethylene, propylene, etc.), and inorganic gasses (e.g. nitrogen, argon, carbon dioxide, carbon monoxide, phosgene, hydrogen, carbonyl sulfide, hydrogen sulfide, etc.).

In the course of the reaction of hydrogen chloride and oxygen, the aromatic chlorohydrocarbons and the aliphatic chlorohydrocarbons are oxidized to generate carbon dioxide, water and chlorine, the aromatic hydrocarbons and the aliphatic hydrocarbons are oxidized to generate carbon dioxide and water, carbon monoxide is oxidized to generate carbon dioxide, and phosgene is oxidized to generate carbon dioxide and chlorine.

As the gas containing oxygen, oxygen or an air is used. Oxygen may be produced by usual industrial methods such as a pressure-swing method of an air, deep-cooling separation of an air, etc.

While the theoretical molar amount of oxygen necessary for oxidizing one mole of hydrogen chloride is 0.25 mole, it is preferable to use oxygen in an amount exceeding the theoretical amount, and more preferably, 0.25 to 2 moles of oxygen is used per one mole of hydrogen chloride. When the amount of oxygen is too low, the conversion of hydrogen chloride may decrease. When the amount of oxygen is too high, it may be difficult to separate formed chlorine from unreacted oxygen.

In the present invention, preferably, the gas containing oxygen is divided into portions and introduced in at least two reaction zones each comprising a catalyst-packed layer, which are arranged in series.

One example of a method for introducing the gas containing oxygen with dividing it into portions is a method comprising introducing the whole volume of the gas containing hydrogen chloride and a part of the gas containing oxygen in the first reaction zone, and introducing the reaction mixture from the first reaction zone and the rest of the gas containing oxygen in the second reaction zone. Herein, the first reaction zone means a reaction zone in which the raw material gas is firstly introduced, while the second reaction zone means a reaction zone in which the raw material gas is introduced subsequent to the first reaction zone. The divided amount

of the gas containing oxygen, which is introduced in the first reaction zone, is from 5 to 90 %, preferably from 10 to 80 %, more preferably from 30 to 60 % based on the whole volume of the gas containing oxygen. When this divided amount is too low, it may be difficult to control the temperature in the second and subsequent reaction zones.

In the present invention, the temperature in at least one of the reaction zones should be controlled with the heat exchange system. Thereby, the excessive hot spot in the reaction zone is suppressed, and the reaction zone is effectively used, so that the stable activity of the catalyst is maintained and chlorine can be stably obtained at a high yield. Accordingly, the catalyst cost, the equipment cost, the operation cost, and the stability and easiness of the operation are maintained at the reasonable levels.

At least two reaction zones each comprising a catalyst-packed layer, which are arranged in series, can be formed by packing at least two kinds of the catalysts in a reactor, or by controlling the temperatures in at least two reaction zones independently. Here, the reaction zone comprising the catalyst-packed layer constitutes a fixed bed reactor, but neither a fluidized bed reactor nor a moving bed reactor.

To pack at least two kinds of the catalysts, the

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catalyst-packed layer in the tubular reactor is divided  
into at least two zones along the axis direction of the  
reactor and catalysts having different activities,  
compositions and/or particle sizes are packed in at least  
5 two zones respectively, or at least two portions of the  
catalyst are diluted with fillers consisting of the  
inactive material and/or the carrier at different dilution  
ratios and packed in at least two zones respectively, or  
the catalyst and the catalyst which is diluted with fillers  
10 consisting of the inactive material and/or the carrier are  
packed in at least two zones respectively.

When the catalyst is diluted with the fillers  
consisting of the inactive material and/or the carrier, the  
entire of the catalyst and the fillers consisting of the  
15 inactive material and/or the carrier means the reaction  
zone comprising the catalyst-packed layer.

In general, two successive reaction zones are directly  
in contact with each other, but the inactive material may  
be packed between the reaction zones. However, the layer  
20 packed with only the inactive material is not regarded as a  
reaction zone.

To independently control the temperatures in at least  
two reaction zones, at least two independent systems may be  
used to control the temperatures. In this case, at least  
25 one of the temperature-control systems should be the heat



exchange system.

Herein, the heat exchange system means a system providing a jacket outside the tubular reactor, which is filled with the catalyst to remove the heat of reaction generated by the reaction with a heating medium in the jacket. With the heat exchange system, the temperature in the reaction zone comprising the catalyst-packed layer in the reactor can be controlled with the heating medium in the jacket. In the industrial process, a shell-and-tube heat exchanger type fixed bed multi-tube reactor may be used, in which tubular reactors, which are arranged in series and have the reaction zones comprising the catalyst-packed layer, are arranged in parallel, and a jacket is provided around the tubular reactors. Besides the heat exchange system, an electric furnace system may be used, but it has a problem such that the temperature control in the reaction zone(s) is difficult.

In the present invention, preferably, the temperatures of at least two reaction zones are controlled with the heat exchange systems. To this end, the heating media are independently circulated in the discrete jackets to independently control the temperatures of the respective reaction zones; or a jacket is divided into at least two sections with partitions and the heating media are independently circulated in the partitioned sections to

control the temperatures of the reaction zones. The partitions may be directly fixed to the tubular reactors by welding, although a gap may be left between each partition and the tubular reactor to an extent that the heating media can be substantially independently circulated. The heating medium in the jacket is preferably flowed from the bottom to the top of the jacket so that the medium has no cavitation therein.

Preferably, the temperatures of all the reaction zones are controlled with the heat exchange systems, since the reaction heat is satisfactorily removed, and the stability and easiness of the operation are maintained.

Examples of the heating medium include molten salts, steam, organic compounds, molten metals, etc. Among them, the molten salt or steam is preferable from the viewpoint of the thermal stability and handling easiness, and the molten salt is more preferable from the viewpoint of the good thermal stability. The molten metal is expensive and difficult to handle. Examples of the composition of the molten salt include the mixture of 50 % by weight of potassium nitrate and 50 % by weight of sodium nitrite, the mixture of 53 % by weight of potassium nitrate, 40 % by weight of sodium nitrite and 7 % by weight of sodium nitrate, etc. Examples of the organic compound include DOWTHERM A (the mixture of diphenyloxide and diphenyl), etc.

As the number of the reaction zone increases, the reaction zones can be more effectively used. From the industrial viewpoint, the number of the reaction zones is usually from 2 to 20, preferably from 2 to 8, more preferably from 2 to 4. When the number of the reaction zones is too large, the kinds of the catalysts packed may increase and/or the number of apparatuses to control the temperature increases so that the process may become less economical.

In the present invention, preferably, the ratio of the first reaction zone to the reaction zones comprising the catalyst-packed layers arranged in series is 70 % by volume or less, more preferably 30 % by volume or less. More preferably, the reaction zones are packed with substantially the catalyst only, the mixture of substantially the catalyst and the inactive material, the mixture of substantially the catalyst and the carrier, or the mixture of substantially the catalyst, the inactive material and the carrier so that the ratio of the first reaction zone is 70 % by volume or less, more preferably 30 % by volume or less and the temperature in the second reaction zone is usually at least 5°C higher, preferably at least 10°C higher than that in the first reaction zone; or that the ratio of the first reaction zone is 70 % by volume or less, more preferably 30 % by volume or less and the

activity in the second reaction zone is usually at least 1.1 times higher, preferably at least 1.5 times higher than that in the first reaction zone; or that the ratio of the first reaction zone is 70 % by volume or less, more preferably 30 % by volume or less, the temperature in the second reaction zone is usually at least 5°C higher, preferably at least 10°C higher than that in the first reaction zone and the activity in the second reaction zone is usually at least 1.1 times higher, preferably at least 1.5 times higher than that in the first reaction zone. Herein, the activity in the reaction zone (mol-HCl/ml-reaction zone·min) means a value obtained by dividing the product of the hydrogen chloride reaction activity per a unit catalyst weight and a unit time (mol-HCl/g-catalyst·min) and the amount of the catalyst filled (g-catalyst) by the volume of the reaction zone (ml-reaction zone). The hydrogen chloride reaction activity per a unit catalyst weight and a unit time is calculated from the amount of chlorine generated when hydrogen chloride and oxygen are reacted by supplying 0.5 mole of oxygen per 1 mole of hydrogen chloride at a ratio of a catalyst volume to a supply rate of hydrogen chloride under the normal state (0°C, 0.1 MPa) in the range between 4,400 and 4,800 h<sup>-1</sup>, under a reaction pressure of 0.1 MPa at a reaction temperature of 280°C.

In the first reaction zone, the reaction rate is high since the concentrations of the reactants, that is, hydrogen chloride and oxygen are high. Therefore, the hot spot is generated on the entrance side of the first reaction zone. On the other hand, the temperature at the exit of the first reaction zone is close to the temperature of a heating medium. When the ratio of the first reaction zone exceeds 70 % by volume, a part of the catalyst-packed layer having a temperature close to that of the heating medium in the jacket increases, and thus the catalyst cannot be effectively used.

The catalyst used in the oxidation reaction according to the present invention may be any known catalyst that is used in the production of chlorine through the oxidation of hydrogen chloride. Examples of such a catalyst include catalysts comprising copper chloride, potassium chloride and various compounds as third components, catalysts comprising chromium oxide, catalysts comprising ruthenium oxide, etc. Among them, the catalysts comprising ruthenium oxide are preferable, and those comprising ruthenium oxide and titanium oxide are more preferable. The catalysts comprising ruthenium oxide are disclosed in JP-A-10-182104 and EP 936 184, and the catalyst comprising ruthenium oxide and titanium oxide are disclosed in JP-A-10-194705 and JP-A-10-338502. The amount of ruthenium oxide in the catalyst

is preferably from 0.1 to 20 % by weight. When the amount of ruthenium oxide is too low, the catalytic activity may be low and thus the conversion of hydrogen chloride may decrease. When the amount of ruthenium oxide is too high, the catalyst may become too expensive.

The shape of the catalyst may be any of conventionally used shapes such as a spherical particle, a cylindrical pellet, an extruded form, a ring form, a honeycomb form, or a granule having a suitable size which is produced by milling of a molded material and sieving thereof. The size of the catalyst is preferably 10 mm or less. When the size of the catalyst exceeds 10 mm, the catalytic activity may deteriorate. Although the lower limit of the size of the catalyst may not be limited, the size of the catalyst is at least 0.1 mm, since a pressure loss in the catalyst-packed layer increases if the size is too small. Herein, the size of the catalyst means a diameter of a sphere in the case of the spherical particle, a diameter of a cross section in the case of the cylindrical pellet, or the largest size of the cross section in the case of other forms.

In the present invention, the reaction zones are preferably packed with substantially the catalyst only, the mixture of substantially the catalyst and the inactive material, the mixture of substantially the catalyst and the carrier, or the mixture of substantially the catalyst, the

inactive material and the carrier so that the thermal conductivity becomes highest in the first reaction zone, more preferably, so that the thermal conductivity in the reaction zones successively decreases from the first  
5 reaction zone to the last reaction zone along the direction of the gas flow.

Here, the last reaction zone means a reaction zone into which the raw material gas is lastly supplied. The thermal conductivity of the reaction zone means that of the  
10 materials packed in the reaction zone.

In the reaction zone on the entrance side of the raw materials, the reaction rate is high and the amount of heat generated by the oxidation reaction is large, since the concentrations of hydrogen chloride and oxygen are high.  
15 Accordingly, the excessive hot spot in the catalyst-packed layer can be suppressed when the catalyst having the relatively high thermal conductivity is filled in the reaction zone(s) on the entrance side.

In the present invention, the reaction zones are  
20 preferably packed with substantially the catalyst only, the mixture of substantially the catalyst and the inactive material, the mixture of substantially the catalyst and the carrier, or the mixture of substantially the catalyst, the inactive material and the carrier so that the activities of  
25 the reaction zones successively increase from the first

reaction zone to the last reaction zone along the direction of the gas flow. Thereby, the temperature difference between the adjacent reaction zones decreases and thus the operation can be easily maintained stable.

5 In the present invention, the reaction zones are preferably packed with substantially the catalyst only, the mixture of substantially the catalyst and the inactive material, the mixture of substantially the catalyst and the carrier, or the mixture of substantially the catalyst, the  
10 inactive material and the carrier so that the activity of the last reaction zone is higher than that of the reaction zone immediately preceding the last reaction zone and the hot spot in the last reaction zone is made lower than that in the reaction zone immediately preceding the last  
15 reaction zone. When the activity of the last reaction zone is lower than that of the reaction zone immediately preceding the last reaction zone, and the hot spot in the last reaction zone is higher than that in the reaction zone immediately preceding the last reaction zone, the  
20 conversion of hydrogen chloride may decrease due to the chemical equilibrium composition, since the reaction to convert hydrogen chloride to chlorine and water through the oxidization of hydrogen chloride with oxygen is an equilibrium reaction.

25 In general, the amount (volume) of the catalyst used



is selected so that a ratio of the volume to the supply rate of hydrogen chloride under the normal state (GHSV) is from 10 to 20,000 h<sup>-1</sup>.

5 The direction of flowing the raw materials in the reaction zone is not limited, and the upward or downward stream may be employed.

10 A reaction pressure is usually from 0.1 to 5 MPa. A reaction temperature is preferably from 200 to 500°C, more preferably from 200 to 380°C. When the reaction temperature is too low, the conversion of hydrogen chloride may decrease. When the reaction temperature is too high, the catalyst component may volatilize.

15 The gas temperature at the exit of the last reaction zone is preferably in the range between 200 and 350°C, more preferably in the range between 200 and 320°C. When the gas temperature at the exit of the last reaction zone exceeds 350°C, the conversion of hydrogen chloride may decrease due to the chemical equilibrium composition, since the reaction to convert hydrogen chloride to chlorine and  
20 water through the oxidization of hydrogen chloride with oxygen is an equilibrium reaction.

In the process of the present invention, the superficial linear velocity of the gas in a column is preferably from 0.2 to 10 m/sec., more preferably from 0.2  
25 to 5 m/sec. When the linear velocity of the gas is too low,

the excessive number of the tubular reactors is necessary to attain the satisfactory throughput of hydrogen chloride with the industrial scale reaction apparatus. When the linear velocity of the gas is too high, the pressure loss in the catalyst-packed layer may increase. Herein, the superficial linear velocity of the gas in the column means a ratio of the total supply rate of all the gases supplied in the catalyst-packed layer under the normal state ( $0^{\circ}\text{C}$ , 0.1 MPa) to the cross sectional area of the tubular reactor.

The inner diameter of the tubular reactor is usually from 10 to 50 mm, preferably from 10 to 40 mm, more preferably from 10 to 30 mm. When the inner diameter of the tubular reactor is too small, the excessive number of the tubular reactors may be required to achieve the satisfactory throughput of hydrogen chloride with an industrial scale reaction apparatus. When the inner diameter of the tubular reactor is too large, the excessive hot spot may be formed in the catalyst-packed layer.

The ratio of the inner diameter ( $D$ ) of the tubular reactor to the size ( $d$ ) of the catalyst ( $D/d$ ) is usually from 5/1 to 100/1, preferably from 5/1 to 50/1, more preferably from 5/1 to 20/1. When the ratio  $D/d$  is too small, the excessive hot spot may be formed in the catalyst-packed layer. When this ratio is too large, the pressure loss in the catalyst-packed layer may increase.

## Examples

The present invention will be illustrated by the following Examples.

### Example 1

5 As a reactor, a fixed bed reactor was used, which consisted of a tubular reactor (with a sheath tube for temperature measurement having an outer diameter of 5 mm) having an inner diameter of 18 mm and a length of 1 m and was equipped with a jacket using a molten salt (potassium  
10 nitrate/sodium nitrite = 1/1 by weight) as a heating medium.

In the upper part of the reactor, 80.2 g (60.0 ml) of an extruded catalyst comprising 6.6 wt. % of ruthenium oxide supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> having a diameter of 1.5 mm was packed to form the first reaction zone. The catalyst was  
15 reused after using it in the oxidation reaction of hydrogen chloride for about 260 hours.

Below the first reaction zone, the mixture of 35.9 g (35.6 ml) of a spherical catalyst comprising 6.6 wt. % of ruthenium oxide supported on anatase crystal TiO<sub>2</sub> having a  
20 diameter of 1 to 2 mm and 37.6 g (17.8 ml) of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles having a diameter of 2 mm (SSA 995 manufactured by NIKKATO Co., Ltd.), which had been well mixed, was packed to form the second reaction zone.

The packed lengths of the catalysts were 0.280 m in  
25 the first reaction zone, and 0.235 m in the second reaction

zone. The packed volumes of the catalyst were 66 ml in the first reaction zone and 55 ml in the second reaction zone, and the volume ratio of the first reaction zone was calculated to be 54 % by volume.

5        The extruded catalyst comprising 6.6 wt. % of ruthenium oxide supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> having a diameter of 1.5 mm was produced as follows:

10        Commercially available  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.), ruthenium chloride, pure water and alumina sol (Alumina Sol 200 manufactured by Nissan Chemical Co., Ltd.) were well mixed. To the mixture, dry air was blown at room temperature to dry the mixture until it had a suitable viscosity. The mixture was extruded in the form of pellets having a diameter of 1.5 mm. Then, the pellets were dried in an air at 60°C for 4 hours. The obtained solid was heated from room temperature to 350°C over one hour, and calcined at the same temperature for 3 hours to obtain the extruded catalyst comprising 6.6 wt. % of ruthenium oxide supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> having a diameter of 1.5 mm.

20        The spherical catalyst comprising 6.6 wt. % of ruthenium oxide supported on anatase crystal TiO<sub>2</sub> having a diameter of 1 to 2 mm was produced according to the method described in JP-A-10-338502.

25        The extruded catalyst comprising 6.6 wt. % of

ruthenium oxide supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> used in this Example had a hydrogen chloride reaction activity per a unit catalyst weight and a unit time of  $1.3 \times 10^{-4}$  mol-HCl/g-cat. $\cdot$ min., which was measured as follows:

5 In a Pyrex glass tubular reactor having an inner diameter of 14 mm (with a sheath tube for temperature measurement having an outer diameter of 4 mm), 4.0 g (3.3 ml) of the catalyst was packed, and the reactor was placed in a molten salt bath at 280°C. Then, hydrogen chloride and oxygen were downwardly passed through the reactor from 10 its top to its bottom at flow rates of 0.26 l/min. (normal state) and 0.13 l/min. (normal state) respectively. After 1.5 hours, the exit gas was collected in an aqueous solution of potassium iodide so that generated chlorine, 15 unreacted hydrogen chloride and generated water were absorbed in the solution, and the amount of chlorine generated and the amount of unreacted hydrogen chloride were measured with the iodometry and the neutralization titration, respectively.

20 The spherical catalyst comprising 6.6 wt. % of ruthenium oxide supported on anatase crystal TiO<sub>2</sub> had a hydrogen chloride reaction activity per a unit catalyst weight and a unit time of  $4.8 \times 10^{-4}$  mol-HCl/g-cat. $\cdot$ min., which was measured in the same manner as in the case of the 25 extruded catalyst comprising 6.6 wt. % of ruthenium oxide

supported on  $\alpha$ - $\text{Al}_2\text{O}_3$  except that the amount of the catalyst was 1.9 g (2.0 ml), and the flow rates of oxygen and hydrogen chloride were 0.16 l/min. (normal state) and 0.08 l/min. (normal state), respectively.

5        The activity in the first reaction zone was  $1.6 \times 10^{-4}$  mol-HCl/ml-reaction zone·min., while that in the second reaction zone was  $3.1 \times 10^{-4}$  mol-HCl/ml-reaction zone·min.

10        Hydrogen chloride-containing gas (hydrogen chloride: 99 % volume or more) and oxygen (oxygen: 99 % by volume) were supplied downwardly in the Ni reactor from its top to its bottom at a flow rate of 6.1 l/min. (normal state) and 3.05 l/min. (normal state) respectively and reacted while maintaining the temperature of the molten salt in the jacket at 326°C. The superficial linear velocity of the  
15        gas was 0.65 m/sec. by calculation. In the first reaction zone, the reaction temperatures were 332°C at the entrance, 335°C at the exit, and 347°C at the hot spot. In the second reaction zone, the reaction temperatures were 335°C at the entrance, 338°C at the exit, and 344°C at the hot  
20        spot.

25        The exit gas from the second reaction zone was collected in an aqueous solution of potassium iodide so that generated chlorine, unreacted hydrogen chloride and generated water were absorbed in the solution. Then, the amount of chlorine generated and the amount of unreacted

hydrogen chloride were measured with the iodometry and the neutralization titration, respectively. The conversion of hydrogen chloride to chloride was 30.6 %.

#### Example 2

5 As a reactor, a fixed bed reactor was used, which consisted of one nickel tubular reactor (with a sheath tube for temperature measurement having an outer diameter of 6 mm) having an inner diameter of 26 mm and a length of 2.0 m and equipped with an electric furnace, and two tubular  
10 reactors (each having a sheath tube for temperature measurement having an outer diameter of 6 mm) having an inner diameter of 18 mm and a length of 2.5 m which was equipped with a jacket using a molten salt (potassium nitrate/sodium nitrite = 1/1 by weight) as a heating medium.  
15 The three reactors were connected in series.

In the tubular reactor having the inner diameter of 26 mm, the mixture of 69 g (60 ml) of an extruded catalyst comprising 6.6 wt. % of ruthenium oxide supported on  $\alpha$ - $\text{Al}_2\text{O}_3$  having a diameter of 1.5 mm and 132 g (60 ml) of  $\alpha$ -  
20  $\text{Al}_2\text{O}_3$  particles having a diameter of 2 mm, which had been well mixed, was packed to form the first reaction zone.

In the first tubular reactor having an inner diameter of 18 mm, the mixture of 300 g (300 ml) of a spherical catalyst comprising 6.6 wt. % of ruthenium oxide supported  
25 on anatase crystal  $\text{TiO}_2$  having a diameter of 1 to 2 mm and

340 g (150 ml) of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles having a diameter of 2 mm, which had been well mixed, was packed to form the second reaction zone.

In the second tubular reactor having an inner diameter of 18 mm, 297 g (294 ml) of a spherical catalyst comprising 6.6 wt. % of ruthenium oxide supported on anatase crystal TiO<sub>2</sub> having a diameter of 1 to 2 mm was packed to form the third reaction zone.

The packed lengths of the catalysts were 0.21 m in the first reaction zone, 1.98 m in the second reaction zone, and 1.37 m in the third reaction zone. The packed volumes of the catalysts were 103 ml in the first reaction zone, 447 ml in the second reaction zone, and 309 ml in the third reaction zone. The volume ratio of the first reaction zone was calculated to be 12 % by volume.

The extruded catalyst comprising 6.6 wt. % of ruthenium oxide supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was produced in the same manner as in Example 1, and it had a hydrogen chloride reaction activity per a unit catalyst weight and a unit time of  $2.5 \times 10^{-4}$  mol-HCl/g-cat.·min., which was measured in the same manner as in Example 1 except that the amount of the catalyst was 4.0 g (3.5 ml).

The activities in the reaction zones were  $1.7 \times 10^{-4}$  mol-HCl/ml-reaction zone·min. in the first reaction zone,  $3.2 \times 10^{-4}$  mol-HCl/ml-reaction zone·min. in the second



reaction zone, and  $4.6 \times 10^{-4}$  mol-HCl/ml-reaction zone·min.  
in the third reaction zone.

Hydrogen chloride-containing gas (hydrogen chloride:  
99 % volume or more), oxygen (oxygen: 99 % by volume) and a  
gas comprising unreacted oxygen from which chlorine had  
been removed (oxygen: 86.0 % by volume, chlorine: 8.9 % by  
volume (calculated), nitrogen: 2.3 % by volume, argon:  
2.7 % by volume, carbon dioxide: 0.1 % by volume) were  
supplied downwardly in the Ni reactor from its top to its  
bottom at a flow rate of 6 l/min. (normal state), 1.13  
l/min. (normal state) and 2.15 l/min. (normal state)  
respectively and reacted under a pressure at the entrance  
of the reactor of 1.19 kg/cm<sup>2</sup>-G (0.22 MPa) while  
maintaining the temperature of the electric furnace at  
342°C and the temperatures of the molten salt in the  
jackets at 345°C and 332°C. The superficial linear  
velocities of the gas were 0.31 m/sec. in the reactor  
having an inner diameter of 26 mm and 0.68 m/sec. in the  
reactors having the inner diameter of 18 mm by calculation.  
The reaction temperatures in the first reactor were 322°C  
at the entrance, 343°C at the exit, and 344°C at the hot  
spot. The reaction temperatures in the second reactor were  
336°C at the entrance, 348°C at the exit, and 362°C at the  
hot spot. The reaction temperatures in the third reactor  
were 325°C at the entrance, 338°C at the exit, and 350°C at

the hot spot.

The gas obtained by the reaction was cooled and then fed to an absorption tower, which was equipped with a tank for pure water, a pump for feeding pure water, a pump for feeding 20 wt. % hydrochloric acid and a pump for circulating hydrochloric acid in the tower. The pure water was fed in the tank for pure water with the pump for feeding pure water at a rate of 15 kg/h (29°C), and allowed in contact with the gas recovered from the top of the absorption tower in the tank for pure water before it was fed to the absorption tower. Then, the pure water was fed to the bottom of the absorption tower from the tank by overflowing. 20 Wt. % hydrochloric acid was fed to the top of the absorption tower at a rate of 0.355 kg/hr (29°C) with the pump for feeding 20 wt. % hydrochloric acid so that hydrochloric acid was in contact with the gas in a countercurrent manner. The solution of hydrochloric acid comprising hydrogen chloride and water in the tower was circulated to the top of the absorption tower with a circulation pump and allowed in contact with the gas in the countercurrent manner. This solution was recovered from the exit of the circulation pump at a rate of 0.736 kg/hr. From the top of the tower, the gas of atmospheric pressure was obtained at 28°C.

The gas obtained from the top of the absorption tower

was supplied to a drying tower with sulfuric acid. The drying tower was equipped with a pump for feeding sulfuric acid. In the drying tower, 98 wt. % sulfuric acid was fed at a rate of 0.145 kg/hr. with the pump for feeding sulfuric acid, and the sulfuric acid in the tower was recovered at a rate of 0.172 kg/hr. by overflowing. After separating mists from the resulting dried gas (containing water of less than 0.05 ml/l) with a mist-separator, the gas was fed to a compressor to pressurize it to 9.25 kg/cm<sup>2</sup>-G (1.01 MPa) and then cooled to -20°C so that it was separated to a liquid comprising chlorine, and a gas comprising unreacted oxygen.

The obtained chlorine contained 98.5 % by volume of chlorine (calculated), 1.1 % by volume of oxygen, 0.17 % by volume of nitrogen, 0.07 % by volume of argon and 0.09 % by volume of carbon dioxide. The gas comprising unreacted oxygen was recycled to the reaction.

#### Effects of the Invention

As explained in the above, according to the present invention, the excessive hot spot in the catalyst-packed layer is suppressed and thus the catalyst-packed layer can be effectively used in the process for producing chlorine comprising oxidizing hydrogen chloride in a gas containing hydrogen chloride with a gas containing oxygen. Therefore,

the activity of the catalyst is maintained stable, and chlorine can be stably obtained at a high yield.

Accordingly, the process of the present invention is an advantageous process for producing chlorine from the  
5 viewpoint of a catalyst cost, an equipment cost, an operation cost, and the stability and easiness of the operation.

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## CLAIMS

1. A process for producing chlorine comprising the step of oxidizing hydrogen chloride in a gas containing hydrogen chloride with a gas containing oxygen in the presence of a catalyst, wherein the oxidation of hydrogen chloride is carried out in at least two reaction zones each comprising a catalyst-packed layer, which are arranged in series, and a temperature in at least one of said reaction zones is controlled with a heat exchange system.

2. The process according to claim 1, wherein at least two reaction zones each comprising a catalyst-packed layer, which are arranged in series, are formed by packing at least two kinds of catalysts in a tubular reactor.

3. The process according to claim 1, wherein at least two reaction zones each comprising a catalyst-packed layer, which are arranged in series, are formed by independently controlling the temperatures of said at least two reaction zones.

4. The process according to claim 1, wherein the temperatures in at least two reaction zones are controlled with a heat exchange system.

5. The process according to claim 1, wherein the temperatures in all the reaction zones are controlled with a heat exchange system.

6. The process according to claim 1, wherein the ratio

of the first reaction zone, in which the raw materials are firstly supplied among at least two reaction zones each comprising a catalyst-packed layer, which are arranged in series, is 70 % by volume or less based on the total volume of all the reaction zones.

7. The process according to claim 1, wherein the reaction zones are packed with substantially the catalyst only, a mixture of substantially the catalyst and an inactive material, a mixture of substantially the catalyst and a carrier, or a mixture of substantially the catalyst, the inactive material and the carrier so that the thermal conductivity becomes highest in the first reaction zone.

8. The process according to claim 1, wherein the reaction zones are packed with substantially the catalyst only, a mixture of substantially the catalyst and an inactive material, a mixture of substantially the catalyst and a carrier, or a mixture of substantially the catalyst, the inactive material and the carrier so that the thermal conductivity in the reaction zones successively decreases from the first reaction zone to the last reaction zone along the direction of the gas flow.

9. The process according to claim 1, wherein the reaction zones are packed with substantially the catalyst only, a mixture of substantially the catalyst and an inactive material, a mixture of substantially the catalyst

and a carrier, or a mixture of substantially the catalyst, the inactive material and the carrier so that the activities of the reaction zones successively increase from the first reaction zone to the last reaction zone along the direction of the gas flow.

10. The process according to claim 1, wherein a gas temperature at the exit of the last reaction zone is in the range between 200 and 350°C.

11. The process according to claim 1, wherein a superficial linear velocity of the gas in the column is from 0.2 to 10 m/sec.

12. The process according to claim 1, wherein the volume of the gas containing oxygen is divided and supplied in the reaction zones.

## ABSTRACT

A process for producing chlorine comprising the step of oxidizing hydrogen chloride in a gas containing hydrogen chloride with a gas containing oxygen in the presence of a catalyst, wherein the oxidation of hydrogen chloride is carried out in at least two reaction zones each comprising a catalyst-packed layer, which are arranged in series, and a temperature in at least one of said reaction zones is controlled with a heat exchange system. According to this process, the stable activity of the catalyst is maintained and chlorine can be stably obtained at a high yield since the excessive hot spot in the catalyst-packed layer is suppressed and the catalyst-packed layer can be effectively used.



# Declaration and Power of Attorney for Patent Application

特許出願宣言書及び委任状

## Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name,

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者(下記の氏名が一つの場合)もしくは最初かつ共同発明者であると(下記の名称が複数の場合)信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PROCESS FOR PRODUCING CHLORINE

上記発明の明細書(下記の欄でX印がついていない場合は、本書に添付)は、

the specification of which is attached hereto unless the following box is checked:

☐ 月 日に提出され、米国出願番号または特許協定条約

☒ was filed on January 19, 2000  
as United States Application Number or  
PCT International Application Number

国際出願番号を とし、

PCT/JP00/00210 and was amended on

(該当する場合) に訂正されました。

(if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

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## Prior Foreign Applications

外国での先行出願

014236/1999

Japan

(Number)  
(番号)

(Country)  
(国名)

(Number)  
(番号)

(Country)  
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(Filing Date)  
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Priority Not Claimed

優先権主張なし

22/January/1999

(Day/Month/Year Filed)  
(出願年月日)

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(Day/Month/Year Filed)  
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(Status: Patented, Pending, Abandoned)  
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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委任状: 私は、下記の発明者として、本出願に関する一切の手続きを米国特許商標局に対して遂行する弁理士又は代理人として、下記のものを指名致します。(弁理士、又は代理人の氏名及び登録番号を明記のこと)

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# Japanese Language Declaration

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